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CORRELATION OF MASS TRANSFER DATA FROM LINDE AIR PRODUCTS COMPANY ON THE ADSORPTION OF KRYPTON ON ACTIVATED CHARCOAL

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OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

TO: F. L. Culler

FROM: J. M. Holmes

SUBJECT: Correlation of Mass Transfer Data From Linde Air Products Company on the Adsorption of Krypton on Activated Charcoal.

An attempt has been made to correlate the mass transfer data from Linde's adsorption laboratory. Results of these calculations show that the data thus far give an excellent correlation using the mathematical equations presented by Hougen and Marshall, Chemical Eng. Progress 43 197(1947).

The above paper gives an equation for the fraction adsorbable vapor remaining in a gas stream from an adsorption bed as a function of time, flow rate, slope of equilibrium curve, position in bed and H_{og}, the height of a transfer unit. This equation is presented in graphical form with the following dimensionless quantities as variables:

$\frac{Y}{Y_o}$ = The fraction of the entering stream that has not been adsorbed at position x in the bed and time τ after starting operation of the bed.

$$b\tau = \frac{cG}{\rho H_{og}} \times \tau$$

where:

c = slope of equilibrium curve gm charcoal / gm carrier gas.

G = Mass flow rate $\frac{gm}{hr\ cm^2}$

ρ = Bulk density of charcoal gm/cc

H_{og} = Height of a transfer unit = cm

τ = Time from start of gas flow, hr.

ax = Number of transfer units = $\frac{x}{H_{og}}$

where:

x = length of bed, cm.

The data from Linde Air Products Company were taken in the following manner. Nitrogen containing 1.5% Krypton was bled through a bed of charcoal at -183°C. until the concentration of the exit gas showed 100 parts per million of krypton by mass spectrometer analysis. The adsorb- nitrogen and krypton were then stripped from the bed and analyzed. A material balance of the system showed that the data checked quite well except for the lowest flow rate of 180 cc/min. This flow rate is recalculated to check the material balance and becomes 118.4 cc/min for this work.

The Linde data also include a static equilibrium determination of the adsorption of krypton on charcoal. The application of the Freundlich theory to these data give the following formula which fits the data quite well:

$$v = 256p^{0.110} \quad (-183°C)$$

where:

v = adsorbate cc/gm

p = pressure over bed in m.m. H_g

The correlation method is as follows:

According to the Hougen and Marshall equation, for $y/yo = 0.00667$ which is the concentration for this case, the value of ax(number of transfer units) becomes approximately 5.40 at $b\tau=0$. The Linde data of time vs. flow rate were then extrapolated on semi log paper (Figure 2) to zero time. The flow rate at which the exit concentration would be 100 p.p.m. at zero time is therefore 420 cc/min. Using the value of 5.4 transfer units, the height of a transfer unit at 420 cc/min becomes 2.036 cm. From this one point and the theory that the H_{og} varies as the 0.51 power of G, the value of H_{og} for any flow rate G, may be calculated.

The above theory was checked by actually calculating H_{og}'s from individual values given in the data. However, Hougen and Marshall assumed a linear equilibrium line for their derivation. For this case, the equilibrium line is far from linear as is shown by the 0.110 exponent in the equilibrium equation. For this calculation, the log mean value of the equilibrium line slope for entrance and exit conditions was used. Next,

for each value of G and τ, the values of $b\tau$ and ax were calculated leaving the value of H_{og} as an unknown. H_{og} was then eliminated by using the ratio $ax/b\tau$. Hougen and Marshall's curves were extrapolated to a value of 0.00667 (Figure 3) and from this curve, another curve was constructed as $ax/b\tau$ vs. ax for the constant $y/yo = 0.00667$ (Figure 4).

From this last curve it was possible to find H_{og} from the determined values of $ax/b\tau$. This was done and the calculated values gave excellent agreement (within 16%) with the original method of determining H_{og} (Figure 5).

The above correlation should therefore apply to any bed, at any flow rate, for a temperature of -183°C. and the same grade of activated charcoal (Columbia Grade CXA).

J. M. Holmes

FOSTER WHEELER CORPORATION

CALCULATION OF H_{og} FROM LINDE DATA

A. Velocity when Br = 0, $= \frac{420 \frac{cc}{min}}{2.1} = 200 \frac{cm}{min}$

No. of transfer Units $\cong$ 5.4 (From Extrapolation)

Height transfer Unit $= \frac{11.0}{5.4} = 2.036$ cm.

$\ln H_{og} = 0.710$ $\qquad \ln V = 5.30$

Theory gives $\frac{\ln H_{og}(1)}{\ln H_{og}(2)} = 0.51 \frac{\ln G(1)}{\ln G(2)}$

$\ln H_{og}(1) = \ln H_{og}(2) \times \frac{\ln V(1)}{\ln V(2)} \times 0.51$

(V proportional to G for standard conditions and N_2 carrier gas).

B. Calculation of G:

Dimensions of Bed

Volume = 23.1 c.c.

Height = 11 cm.

Area = 2.1 cm^2

Diameter = 1.64 cm.

Density of Carbon $= \frac{10 \text{ gm}}{23.1 \text{ cc}} = 0.433$ gm/cc.

C. True flow from material balance for observed flow of 180 cc/min.

$$\frac{2930 \text{ cc Kr}}{27.5 \times 60 \text{ min}} \times \frac{1}{0.015} = 118.4 \text{ cc/min}$$

D. Mass Flow Rate (At Standard Conditions)

$$G = \text{Flow } \frac{cc}{min} \times \frac{60\ min}{hr} \times \frac{1}{2.1\ cm^2} \times \frac{mole}{22{,}400\ cc} \times 28\ \frac{gms}{mole}$$

$$= 0.0358 \times \text{Flow } \frac{cc}{min}$$

Flow cc/min	G $\frac{gms}{hr\ cm^2}$	Velocity through Empty Tube cm/min
118.4	4.23	56.4
230	8.22	109.5
270	9.64	128.6
320	11.42	152.4

E. Equilibrium Constant C

$$C = \text{Slope Equilibrium Line}$$

$$= \frac{gm\ Kr/gm\ Gas}{gm\ Kr/gm\ charcoal}$$

$$= \frac{\frac{83.7}{28 \times 760} \times \text{Press. Kr(m.m.)}}{\frac{v\ (cc/gm)}{267.6}} = 1.053\ \frac{p}{v}$$

F. Formula for Kr on Charcoal at -183°C.

$$v = 256P^{0.110}$$

Partial Press. Kr. entering

$$= 0.015 \times 760 = 11.4\ mm$$

$$v = 256(11.4)^{0.110} = 334\ cc/gm.$$

Partial Press. Kr. leaving at end of run.

$$= 100 \times 10^{-6} \times 760 = 0.076\ mm$$

$$v = 256(0.076)^{0.110} = 193\ cc/gm$$

$$C_1 = 1.053 \times \frac{11.4}{334} = 0.03594$$

$$C_2 = 1.053 \times \frac{0.076}{193} = 0.000415$$

$$\text{log mean } C = \frac{0.03594 - 0.00042}{\ln \dfrac{0.03594}{0.000415}} = 0.00796$$

G. Calculation of $b\tau$

$$br = \frac{CG}{\rho \times H_{og}} \times \text{time}$$

$$= \frac{0.00796\ G\ \tau}{0.433 \times H_{og}} = 0.0184\ \frac{G}{H_{og}}\ \tau$$

$$\frac{ax}{b\tau} = \frac{11/H_{og}}{\tau \times 0.0184\ G/H_{og}} = \frac{598}{G \times \tau}$$

H. Determination of H_{og}

Flow	G	Time	ax/br	ax	H_{og}
118.4	4.23	27.5	5.14	8.90	1.24
230	8.22	11.0	6.62	7.80	1.41
270	9.64	8.5	7.30	7.40	1.49
320	11.42	5.25	9.98	6.26	1.76

I. Check of H_{og} with Calculated Value

When Br = 0 $\quad$ $H_{og} = 2.036$

V = 200

$H_{og} = 2.036 \left(\frac{V}{200}\right)^{0.51}$ (V proportional to G for standard conditions and N_2 carrier gas).

Flow	Velocity	Extrapolated H_{og}	Hog Determined	% Deviation
118.4	56.4	1.07	1.24	16%
230	109.5	1.50	1.41	6%
270	128.6	1.62	1.49	8%
320	152.4	1.77	1.76	1%

Adsorption Mass Transfer Data - Linde Air Products Company

From Report 5/4/51

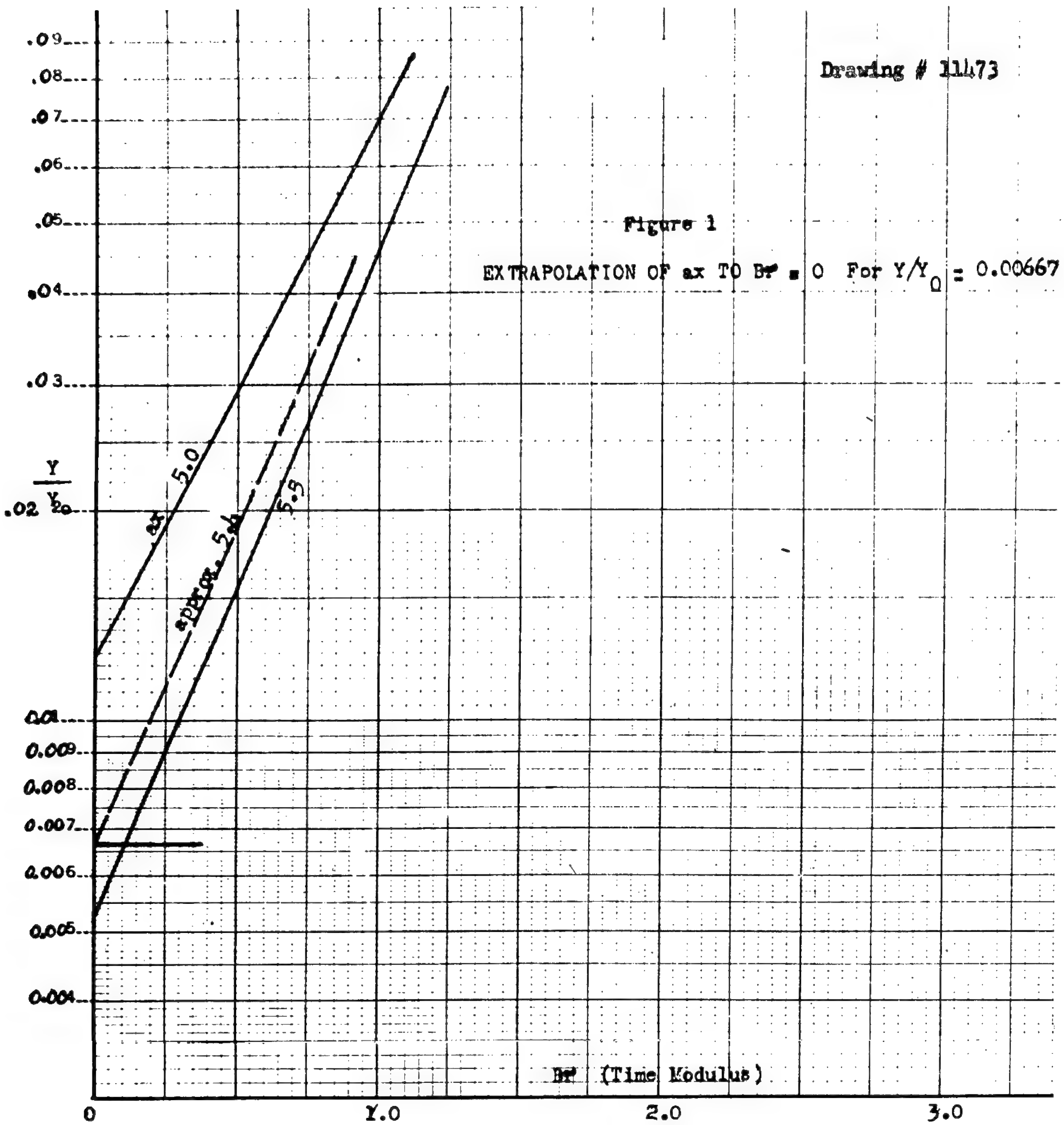
Central Files 51-5-58

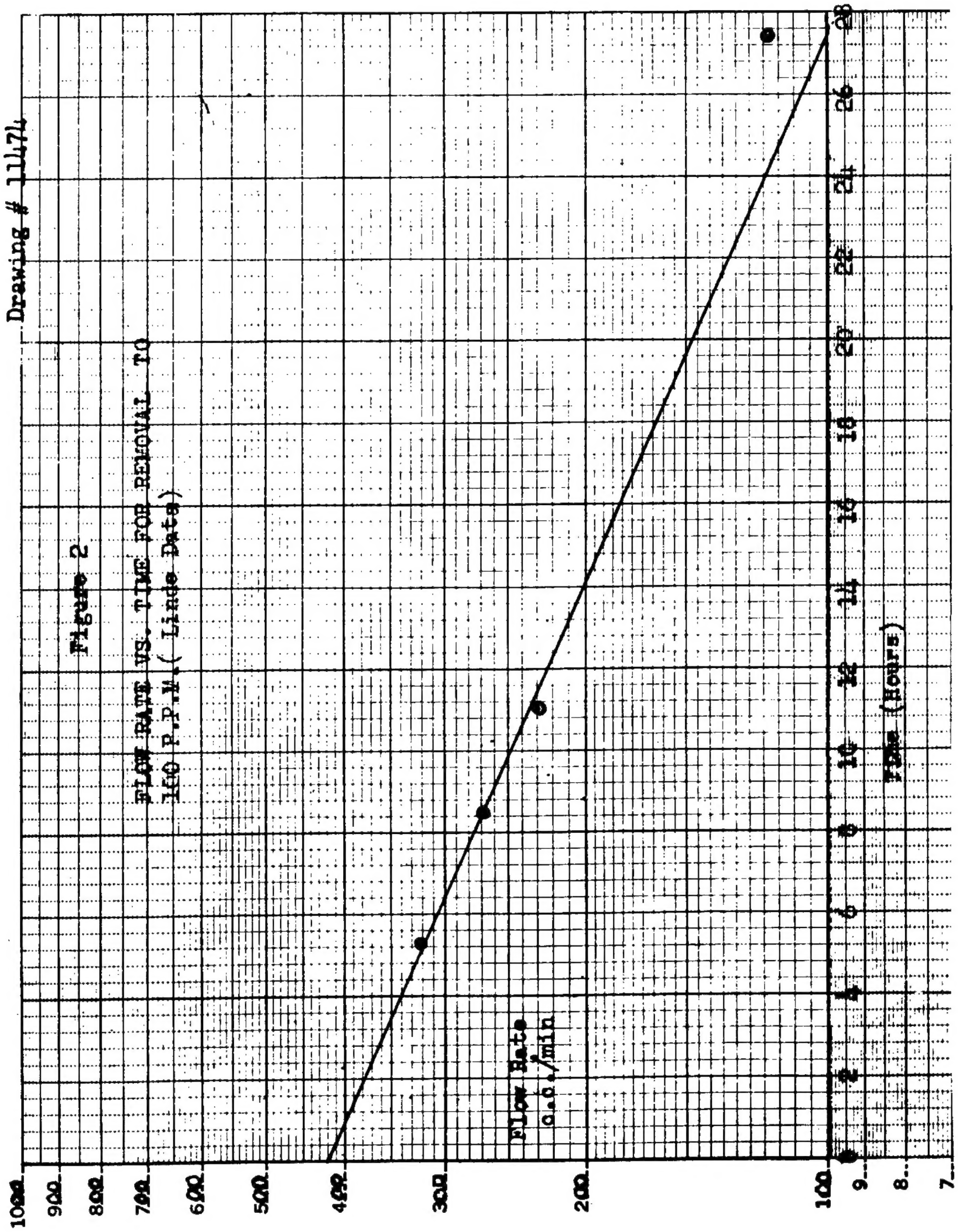
TABLE I

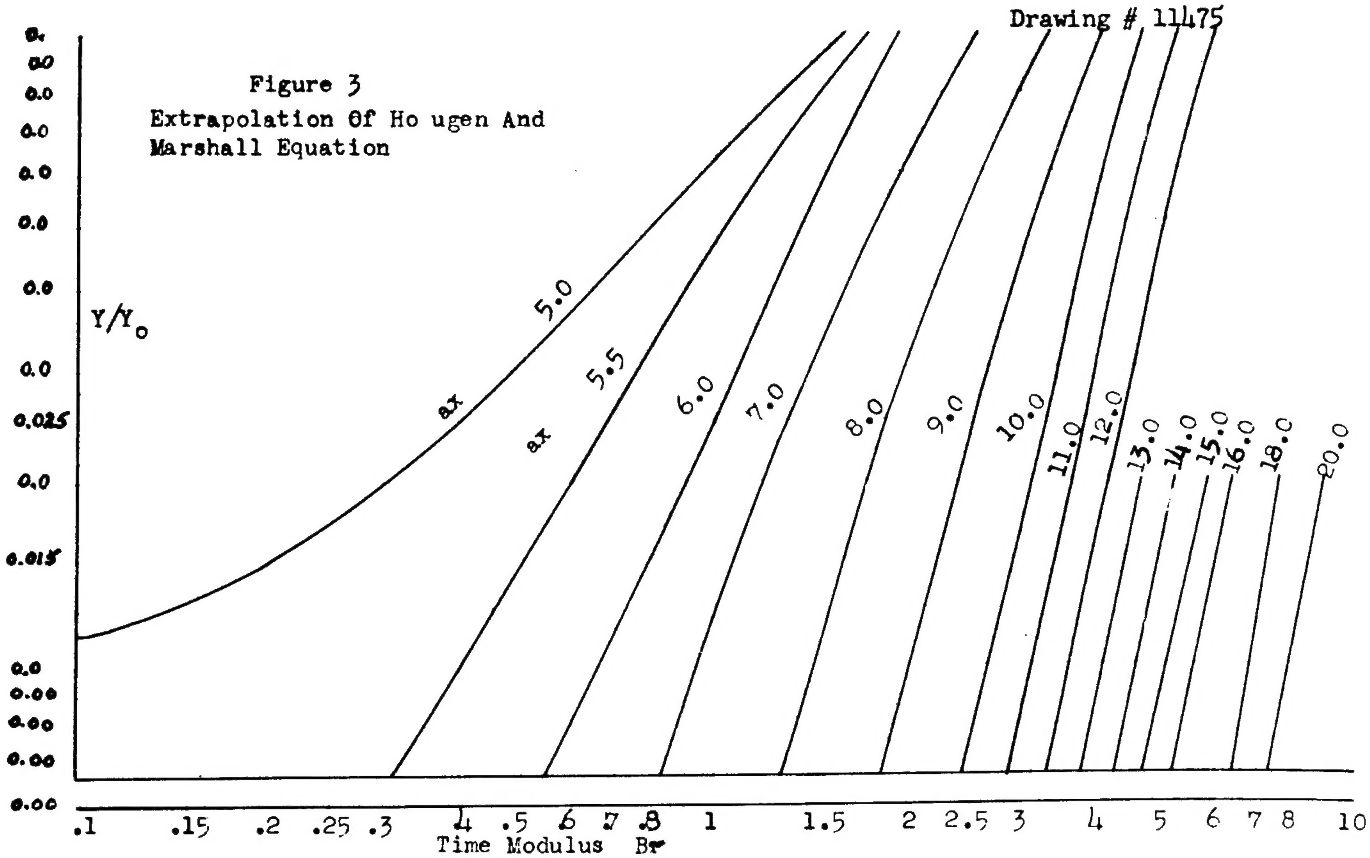
Input Flow	Time to reach 0.01% Krypton in exit gas	Volume of desorbed gas from trap.	Mass spectrometer Analysis of Desorbed Gas	Capacity of trap for Total Gas	Linear Velocity of sample thru empty trap	Time of Contact
180 cc/min.	27-1/2 hrs.	3660 cc.	80% Kr. 20% N_2	366 cc/gr.	1.43 cm/sec.	7.7 sec.
230 "	11 "	3610 cc.	62.5% Kr. 37.5% N_2	360 "	1.82 "	6.0 "
270 "	8-1/2 "	3685 cc.	66% Kr. 34% N_2	369 "	2.15 "	5.1 "
320 "	5-1/4 "	Not measured	-----	----	2.55 "	4.3 "

TABLE II

Input Flow	Time to reach 0.01% Kr. in Exit Gas	Volume of Kr. thru Inlet meter	Volume of Kr. in Desorbed trap
180 cc/min (118 corrected)	27-1/2 hrs.	4450 cc.	2930 cc.
230 cc/min	11 "	2277 cc.	2275 cc
270 "	8-1/2 "	2066 cc.	2430 cc.
320 "	5-1/4 "	1515 cc.	------


Drawing # 11473
Figure 1
EXTRAPOLATION OF ax TO Bτ = 0 For Y/Y0 = 0.00667
.09
.08
.07
.06
.05
.04
.03
.02
Y/Y0
0.01
0.009
0.008
0.007
0.006
0.005
0.004
ax 5.0
approx. 5.4
5.5
Bτ (Time Modulus)
0
1.0
2.0
3.0


Drawing # 11474
Figure 2
FLOW RATE VS. TIME FOR REMOVAL TO
100 P.P.M. (Linde Data)
Flow Rate
c.c./min
Time (Hours)
1000
900
800
700
600
500
400
300
200
100
9
8
7
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28



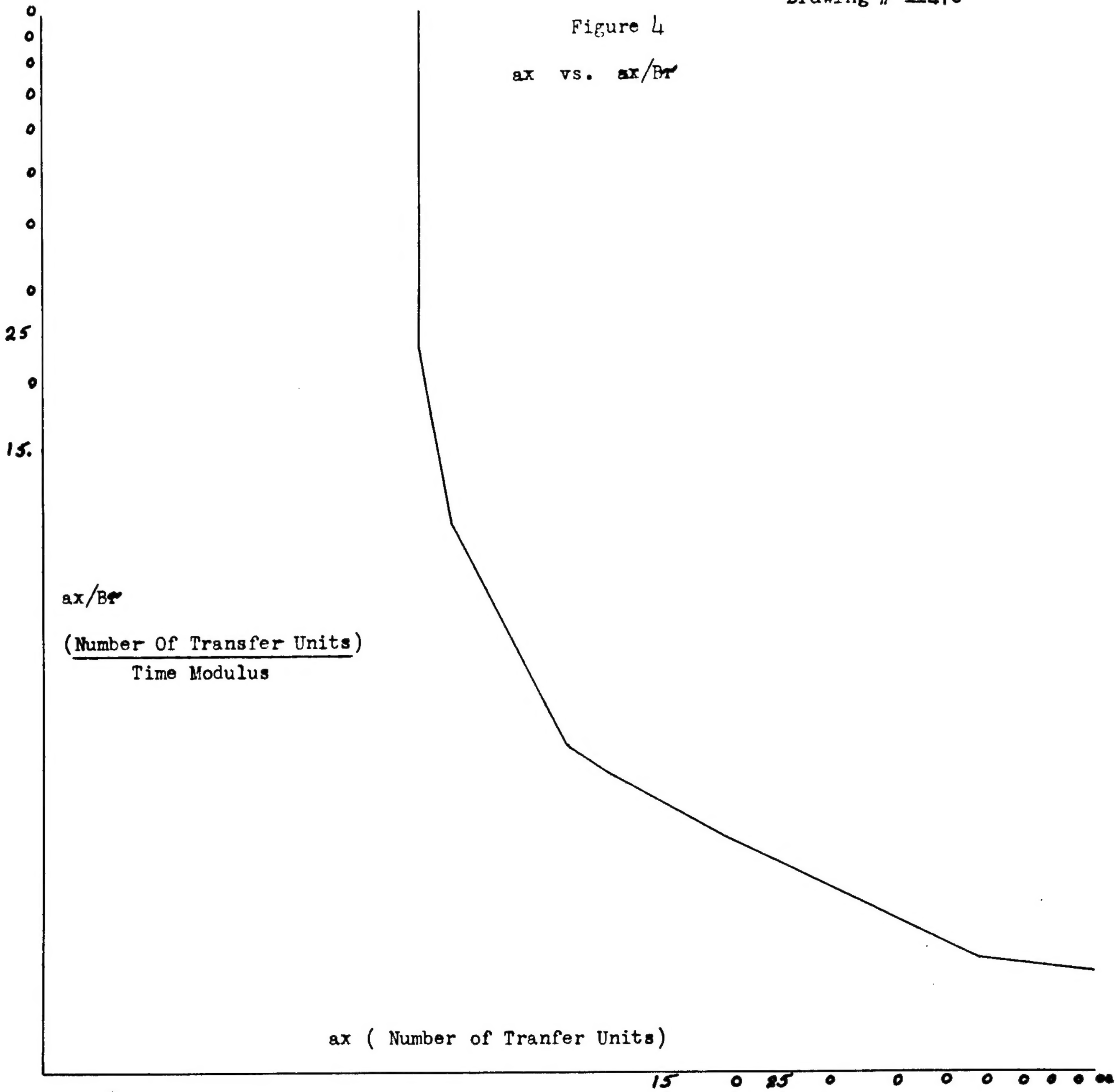
Data For Y/Y_o = 0.00667

ax	Bτ	ax/Bτ
5.5	.318	17.30
6.0	.550	10.91
7.0	.820	8.54
8.0	1.28	6.25
9.0	1.82	4.95
10.0	2.42	4.13
11.0	2.85	3.86
12.0	3.30	3.64
13.0	3.70	3.51
14.0	4.20	3.33
15.0	4.60	3.26
20.0	7.24	2.76
40.0	20.0	2.00
60.0	36.5	1.64
80.0	50.0	1.60
100.0	64.5	1.55

Drawing # 11476

Figure 4

ax vs. ax/Br



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